Short-Pulse Techniques

Part 2 - Perturbation Times in Alkali-Halide Systems

B. J. PIERSMA, SIGMUND SCHULDINER, AND T. B. WARNER

Electrochemistry Branch
Chemistry Division

January 17, 1967

NAVAL RESEARCH LABORATORY
Washington, D.C.

Previous Report in this Series

"Short-Pulse Techniques, Part 1 - Kinetics of the Triiodide/Iodide Reaction on a Platinum Electrode in Neutral Solution," S. Schuldiner and C. H. Presbrey, Jr., NRL Report 5978, Aug. 20, 1963

CONTENTS

ABSTRACT

A new technique involving the perturbation of a system from equilibrium using very short galvanostatic pulses and miniature cells has been applied to study of the electrical double layer at Pt electrodes. The perturbation time, the time required for the double layer to begin charging, was determined for hydrogen- and alkali metal-halide systems and for reversible hydrogen systems in several acids and NaOH. The perturbation time was essentially independent of charging-current density and of the anion in solution but was strongly dependent on the cation species and electrolyte concentration. Models to explain the absence of electrode polarization during the initial flow of charge into the double layer are discussed. A model which involves a very fast Faradaic process and which is consistent with the experimental observations is proposed. It is suggested that the perturbation time, which is less than 100 nanosec for 1 M solutions, represents the time required for movement of ions into or out of the compact double layer.

PROBLEM STATUS

This is an interim report on one phase of the problem; work on this problem is continuing.

AUTHORIZATION

SHORT-PULSE TECHNIQUES

PART 2 — PERTURBATION TIMES IN ALKALI-HALIDE SYSTEMS

B. J. Piersma,* Sigmund Schuldiner and T. B. Warner

Electrochemistry Branch
Chemistry Division

INTRODUCTION

In a previous paper (1), a galvanostatic short-pulse technique was developed to study the kinetics of the I_3^-/I^- reaction on a Pt electrode. Oscilloscopic traces at very short times (less than 0.1 μsec) showed delays or perturbation times in the charging of the electrical double layer from the equilibrium potential. It was suggested that a short-pulse technique could be applied to determine the perturbation times of ions in the compact double layer. This study was undertaken to explore this possibility further.

EXPERIMENTAL SETUP

The miniature glass cells used (Fig. 1) were designed to be terminated coaxial cables. This arrangement minimized the effects of overshoot and ringing inherent in short-pulse measurements. Two central Pt wires, approximately 1 cm long and 0.025 cm diameter, were less than 0.05 cm apart and served as the working and reference electrodes. The counter electrode was a Pt gauze cylinder of size approximately the inside dimensions of the cell, about 1 cm diameter, 1 cm length (Fig. 1). Two 22-gage Teflon tubes, one of which was supplied with a female luer fitting, were sealed in the cell with polyethylene. Solution was added or removed with a gas-tight syringe (Hamilton Model 1001). Gas was bubbled through the cell from a glass pipe system connected to the cell with a male luer fitting.

The basic circuit is similar to that used previously (1,2), and is shown in Fig. 2. The cell was mounted in an aluminum chassis which was attached directly to the pulse generator (E-H Research Laboratories, Inc., Model 121) with a BNC connector. The leads from the cell to BNC connectors on the chassis were made as short as possible, being only a few millimeters long. Since changes in electrolyte concentration varied the solution resistance, the terminating resistor and load resistor were changed such that the output impedance of the pulse generator was matched and the cell IR drop was not excessive. The 200-ohm resistor connected to the reference electrode reduced ringing and overshoot by balancing the impedance in the cable to the oscilloscope. Measurements were made with a Tektronix Type 585 oscilloscope. Long current pulses to examine system cleanliness were obtained with an Electro-Pulse Model 3450D pulse generator (3).

---

*National Academy of Sciences - National Research Council Postdoctoral Research Associate while at NRL. Presently employed at Eastern Baptist College, St. Davids, Pennsylvania, 19089.
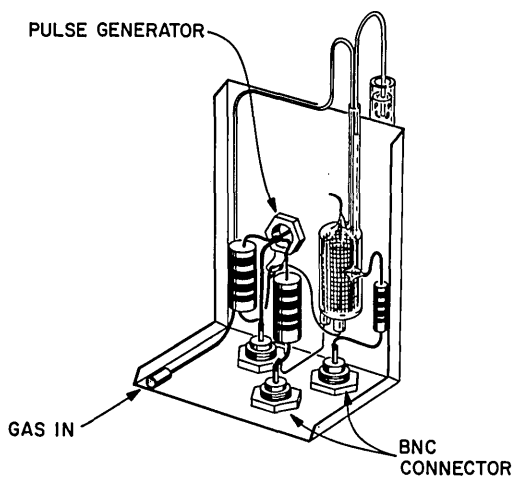
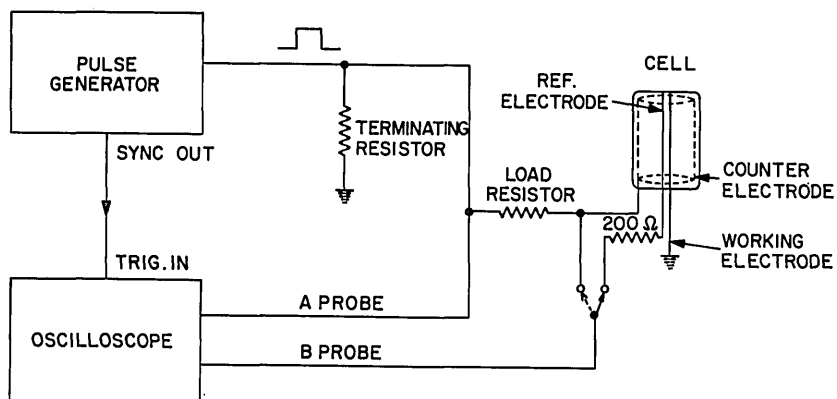Fig. 1 - Miniature cell

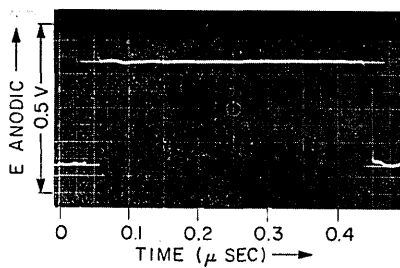Fig. 2 - Block diagram of basic electrical circuit

Fig. 3 - Form of an acceptable pulse across a purely resistive dummy circuit

Values of the charging currents were determined by a method outlined previously (1). The shape of the pulse itself was constantly checked using a dummy circuit with only resistive components. A typical trace of an acceptable pulse is shown in Fig. 3. During the course of the experiments the pulse generator required periodic adjustments to retain the flatness of the pulse and the short rise times (4 nanosec). The experimental technique was also carefully examined using dummy cells with known resistive and capacitative components to completely insure that the perturbation times observed with the electrolytic cells were not instrumental artifacts.

The purification systems for hydrogen and helium were as described previously (4). Chlorine was Matheson, research grade, and was used without further purification. Other reagents were as follows: KI, I_2, KBr, Br_2, LiCl, NaCl, KCl, NaOH, HCl, H_2SO_4, and HNO_3 all "Baker Analyzed" reagent; RbCl and CsCl were prepared from hydroxide solutions by reaction with HCl and recrystallized. All solutions were prepared with triply distilled H_2O (4). All systems were at equilibrium at open circuit.

After the cell had been suitably cleaned,* solution was added and He (in chloride systems Cl_2 was substituted) was bubbled through the cell, for about one hour, to reduce the oxygen concentration in the system. Gas flow was stopped during the few seconds required for measurements because of the large effects of gas bubbles on the cell resistance. Pulses were applied repetitively at rates of 100 to 500 cps. For the pulses used (less than 0.5 μsec) this spacing was sufficient (1), so that the electrodes were at equilibrium at the onset of each perturbation.

RESULTS

Initial studies were carried out with KI solutions containing 0.0025 M I_2 for comparison with previous results (1). Typical charging curves for anodic and cathodic pulses are given in Fig. 4. As the concentration of the KI solution was decreased, the cell resistance increased, and the terminating and load resistors were changed to keep the IR drop within the limits of the oscilloscope screen at the more sensitive amplitude ranges (0.1 to 0.5 v/cm). The effect of changing the charging current on the perturbation time was examined carefully for the KI/I_2 system.

After the KI/I_2 system had been thoroughly examined, KBr/Br_2 and KCl/Cl_2 systems were studied in a similar manner. For the latter system, Cl_2 rather than an inert gas was bubbled through the cell. The study was then extended to MCl/Cl_2 systems with different cations and to reversible hydrogen systems with several electrolytes. All of the systems examined were reversible to provide stable base potentials. In an attempt to obtain a clean cell with an H_2SO_4/H_2 system after KI/I_2 solutions had been used, it was found, by using the reported cleanliness tests (3), that it was extremely difficult to remove all traces of iodide from the Pt electrodes. It was thus necessary to use different cells for the different halides and for the acid/H_2 systems studied. In light of these results, the recent suggestion by Devanathan and Tilak (5) of treating Pt electrodes with KI solution prior to capacity measurements to obtain a base capacity of 20 $\mu F/cm^2$ would seem open to question. This treatment might explain the difference in their results from those obtained in this laboratory (4); i.e., a capacity of 40 $\mu F/cm^2$ was obtained with bright Pt, in the so-called double-layer region of potentials, in a highly purified system, containing H_2SO_4.

---

*The cleaning procedure included: (a) warm (approx. 60° C) concentrated NaOH solution, (b) warm conc. HNO_3, (c) warm 50% HNO_3/50% H_2SO_4, (d) 10 to 12 rinses with triply distilled H_2O over a period of 24 hours. Each step was followed with 10 to 12 rinses with triply distilled H_2O.
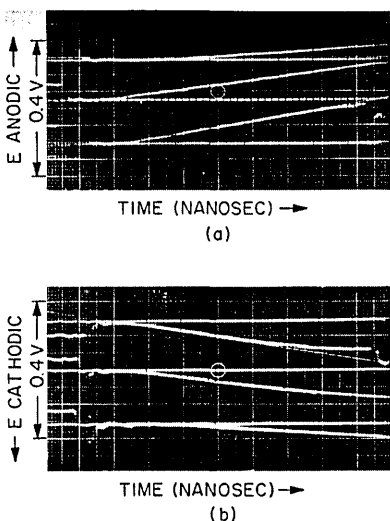
TIME (NANOSEC) →

(a)

TIME (NANOSEC) →

(b)

Fig. 4 - Oscilloscope traces of pulses in I M KI/ 0.0025 M I_2 systems, i = 2.2 A/cm². Each major division = 1 cm on oscilloscope screen. a. Anodic pulses, time scales: lowest trace 50 nanosec/cm, middle trace 40 nanosec/cm, upper trace 20 nanosec/cm. b. Cathodic pulses, time scales: lowest trace 20 nanosec/cm, middle trace 40 nanosec/cm, upper trace 50 nanosec/cm.

The effect of changing the charging current on the perturbation time in the 1.0 M KI/0.0025 M I_2 system is presented in Table 1, together with the double-layer capacitance. These data are representative of the reproducibility obtainable with this technique. The perturbation times were determined from the oscilloscope traces in two different ways. As seen from Fig. 4, the perturbation time is readily obtained by simply measuring the time between the onset of the pulse and the point at which double-layer charging begins. Alternatively, the IR drop was measured at pulse cutoff, and this value was marked off from the initial foot of the pulse. The time at which the polarization, due to charging of the double layer, became larger than this IR drop was taken as the perturbation time. Identical perturbation times were obtained with these two procedures, within the scatter of measurements, being in general ±3 nanosec. Scatter of data in more dilute solutions in some cases became as large as ±10 nanosec. Here the smaller charging currents used (because of higher solution resistance) resulted in slower charging of the double layer. Since perturbation times were also longer in the more dilute solutions, the scatter was always less than ±10 percent. With more dilute solutions, the IR correction method was more precise, since a sharp break due to double-layer charging was not obtained. Close examination of oscilloscope traces at every current density used (0.1 to 5 amp/cm²) indicates small transition regions before double-layer charging becomes linear.

Table 1
Perturbation Times and Double Layer Capacitances at Different Current
Densities for 1.0 M KI/0.0025 M I Solution

Current Density (A/cm²)	Cathodic Pulse		Anodic Pulse	
	t_p (nanosec)	C_{dl} (μF/cm²)	t_p (nanosec)	C_{dl} (μF/cm²)
1.65	75	6.3	85	7.5
2.49	74	7.1	83	8.3
3.09	76	6.1	80	7.3
3.34	74	6.4	82	6.9
4.76	75	7.3	84	8.6
Averages	75 ± 1	6.6 ± 1	83 ± 3	7.7 ± 1

The variation of perturbation time, t_p, with concentration is shown in Fig. 5, for KI/I_2, KBr/Br_2, and KCl/Cl_2 systems. It is evident that: (a) a good linear relation between the perturbation time, t_p, and log concentration is obtained, (b) anodic pulses result in different perturbation times from cathodic pulses (however, t_p becomes the same at a salt concentration of about 5 M), and (c) changing the anion has surprisingly little influence on t_p. Further experiments to examine the influence of the nature of the anion on t_p are summarized in Table 2. It is evident that the anion has very little to do with the perturbation times observed.
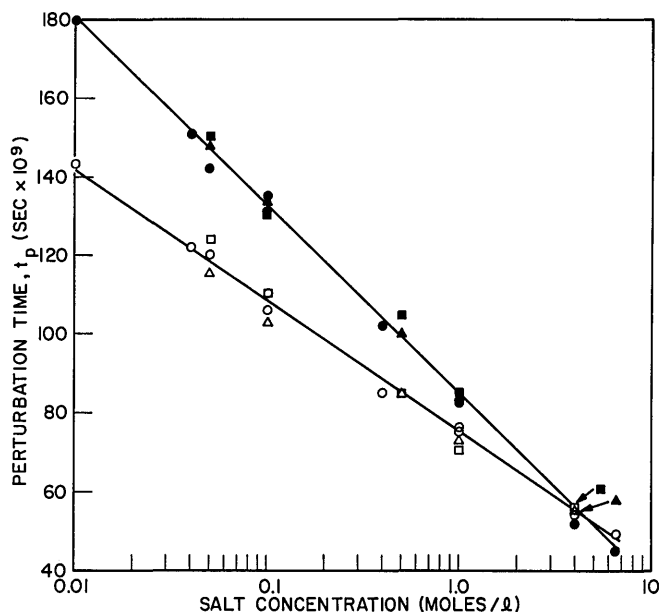

Fig. 5 - Perturbation time t_p vs log conc. for KI/I_2 O cathodic, ● anodic, KBr/Br_2 △ cathodic, ▲ anodic and KCl/Cl_2 □ cathodic, ■ anodic systems

Table 2
Perturbation Times in Reversible Hydrogen Systems

1 M Solutions	t_p, Cathodic (nanosec)	t_p, Anodic (nanosec)
H_2SO_4	19	38
HNO_3	18	36
HCl	20	40
NaOH	70	78

The variation of t_p with concentration of MCl/Cl_2 systems with different cations is given in Fig. 6 and 7 for anodic pulses and cathodic pulses respectively. In addition to the linear t_p vs log conc relations and the differences between $t_{p,a}$, anodic and $t_{p,c}$, cathodic,

a rather startling dependence on the cation is observed. The largest difference is between H^+ and the first alkali metal ions Li^+, while the higher alkali metal ions, K^+, Rb^+, and Cs^+, give similar behavior.
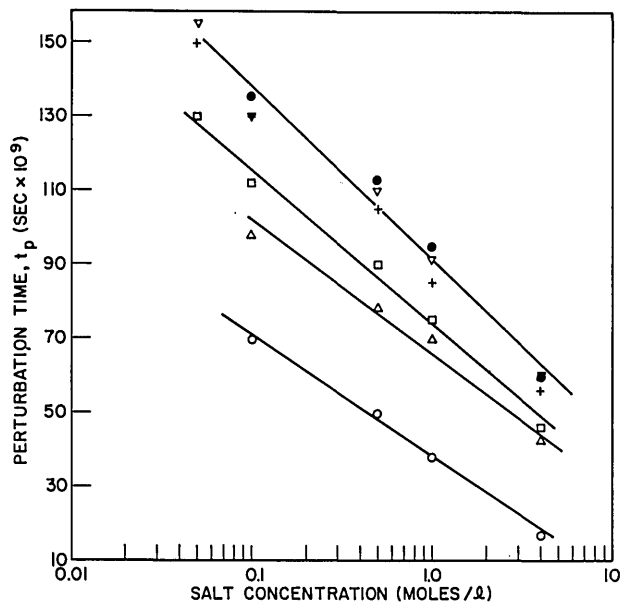
Fig. 6 - Perturbation time t_p vs log conc. from anodic charging in MCl/Cl_2 systems; O H^+, △ Li^+, □ Na^+, + K^+, ▽ Rb^+, ● Cs^+
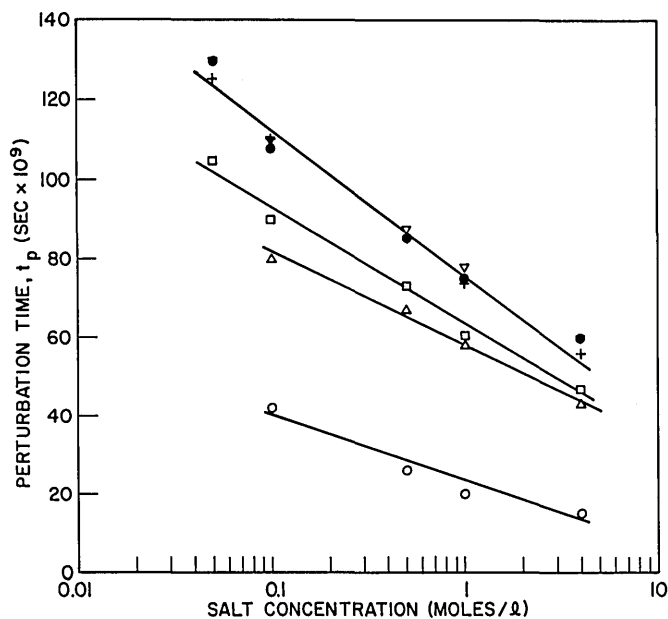
Fig. 7 - Perturbation time t_p vs log conc. from cathodic charging in MCl/Cl_2 systems; O H^+, △ Li^+, □ Na^+, + K^+, ▽ Rb^+, ● Cs^+

DISCUSSION

The experimental observations which must be considered in discussion of the perturbation times are summarized as follows:

1. $t_p \neq f(i)$ within the limits of i used (0.1 to 5 A/cm^2)

2. $t_p \neq f(E_{rev})$

3. $t_p = f(cation)$, $t_{p,H^+} < t_{p,Li^+} < t_{p,Na^+} < t_{p,K^+} \approx t_{p,Rb^+} \approx t_{p,Cs^+}$

   $t_p \neq f(anion)$, $t_{p,SO_4} = \approx t_{p,NO_3^-} \approx t_{p,Cl^-} \approx t_{p,Br^-} \approx t_{p,I^-}$

4. $\dfrac{dt_p}{d \log conc.} = -const.$, $\left(\dfrac{dt_{p,a}}{d \log conc.}\right) > \left(\dfrac{dt_{p,c}}{d \log conc.}\right)$

5. $t_{p,a} > t_{p,c}$ for conc. < 4 M

   $t_{p,a} \approx t_{p,c}$ for conc. > 4 M

A prime consideration for a model to explain the perturbation time is the fact that energy is being passed into the double layer while the measured potential difference across the double layer remains constant. The observations tend to indicate that two processes are involved, i.e., one which is time dependent but independent of the charging current and which determines t_p, and another which can use the charge passed during t_p without altering the potential difference, i.e., without charging the double layer.

The latter process can be understood on a physical basis from the equation for a capacitor, if we assume that the double layer does act essentially as an ideal unit-area capacitor:

$$C = \frac{Q}{E} = \frac{\epsilon}{4\pi d}$$

where the dielectric constant in the double layer $\epsilon \approx 6$ and the distance d, normally the distance between the plates of a capacitor, is equated to the thickness of the compact layer and is approximately 3.5 Å. To obtain constant E while Q changes required either a change in the dielectric constant, ϵ, or a change in the double-layer thickness, d, i.e., a change in position of the outer Helmholtz plane. If we assume for E = 0.6 V, that Q = 10 μcoul/cm^2 and d = 3.5 Å, then ϵ = 6.6. Hence, for a typical change in Q from an anodic pulse of 1 A/cm^2 during a perturbation time of 100 nanosec, which gives a 1 percent increase in the total charge across the double layer (10 μcoul/cm^2 to 10.1 μcoul/cm^2), $\Delta \epsilon$ = 0.06; i.e., the dielectric constant would have to increase by about 1 percent to give the required result. Alternatively, if we assume constant ϵ, the thickness d would have to decrease by about 1 percent during the anodic perturbation time. Whether ϵ and d would have to increase or decrease would of course depend on the potential with respect to the potential of zero charge, p.z.c., i.e., whether Q increases or decreases. In any case, the changes required are on the order of 1 percent which seems entirely reasonable.

A more detailed model is obtained by examining the chemical nature of a change in ϵ or a change in d. The dielectric constant is increased by removal of ions from the double layer, either by mass transfer or by neutralization through charge transfer, or by a relaxation of restriction on the movement of dipoles. Since a net transfer of ions into or out of the double layer would result in actual charging of the capacitor, i.e., a change in E with Q, this cannot occur during the perturbation time. Further, the time required for ions to move into or out of the double layer is very possible on the same order as the observed perturbation times. Grahame (6) has suggested, from calculations for a simple RC circuit and based on data from a mercury electrode, that the time required for establishment of ionic equilibrium within the double layer is on the order of 100 nanosec.

The double-layer thickness is changed by a shift of the outer Helmholtz plane. This shift could occur by a slight relaxation of the plane, e.g., by a movement of the cations within their solvation sheaths. The kinds of shifts involved, i.e., about 0.05 Å, could readily be achieved simply by a movement of the cations within the sheaths of water molecules surrounding them, and as such do not require movement of ions into or out of the double layer.

The perturbation time can be viewed either as the time required for the transfer of ions, i.e., a type of inertia which must be overcome before ions can begin to move, or as the time required to saturate some initial process in the compact layer, e.g., dielectric saturation, before the effects of the charging pulse are communicated to the diffuse layer and the bulk of the solution. By this we mean that either the ions require a finite time, i.e., t_p, before they can begin to move, quite analogous to the relaxation times observed in solution, or that they can respond at faster times but that some initial process must be first satisfied. Any consistent model must include the cation dependence and anion and charging current independence of the perturbation times. The process which accepts energy without changing the potential difference across the double layer could involve dipole rotation or orientation, a movement of electrical center of ions in the outer Helmholtz plane, or an electron-transfer process with the transfer of an equivalent number of oppositely charged ions out of or into the compact layer (or possibly only the shift of the outer Helmholtz plane), the charge on the electrode remaining effectively constant. These processes are very likely not separable, but for purposes of argument we shall discuss them separately.

From the frequency dependence of the double-layer resistance and capacitance at solid electrodes measured by ac impedance methods, Bockris and coworkers (7,8) proposed a relaxation time for water dipoles. To explain relaxation times of about 10^{-8} sec on Hg and about 10^{-6} sec on Cu in primarily sulfate solutions, they assumed that water molecules which are adsorbed upon the electrode are restricted in motion so that their relaxation time is made large enough for it to fall within the frequency range of measurement. The relaxation of water dipoles at the copper-solution interface was considered as qualitatively resembling that in ice, with a relaxation time of 10^{-3} sec, rather than that in water, 10^{-10} sec. A slow relaxation process in the oriented water layer at charged interfaces has also been proposed from the effects of superimposing an ac field over a dc polarizing potential at a dropping mercury electrode (9).

Another indication of the times involved in the motion of water dipoles can be taken from water-water exchange rates (10). The substitution rates of the first-hydration-shell water molecules by ligands for alkali-metal cations have been reported for Li^+ as 0.47 to 9.0×10^8 per sec and for Cs^+ as 2.1 to 50×10^8 per sec. The water molecules held in the first hydration shell, particularly for Li^+, should be somewhat analogous to water oriented in the double layer. It would appear that the times involved for the rotation and orientation of water dipoles in the double layer agree reasonably well with the observed perturbation times. The influence of cations on the perturbation time may be attributed to hydration and to the effect of ordering of the water dipoles in the compact layer by the cations. A correlation of the perturbation times with hydration number (11) is shown in Fig. 8. In this case the change in t_p with concentration has been plotted, since this is a constant for each cation. It is interesting to note that if this correlation is correct, the hydration number for H^+ is between 5 and 6. Initially it would appear that the cation effect of t_p is in the wrong direction. For example, following the suggestion of Samoilov (12) that the larger cations (K^+, Rb^+, and Cs^+) have a negative hydration number, i.e., are structure breaking, the rotation of water dipoles would be expected to be easier and thus faster for these cations. However, if we view the process as one which must become saturated, i.e., completed, before double-layer charging begins, then the least oriented systems should require more time to become fully oriented. For example, the double layer with Li^+ would be expected to have a more ice-like water structure than a double layer with Cs^+. Thus it should require less time for the dipoles to become completely oriented in the field in the presence of Li^+, since a higher degree of order is already established. Of course the water dipoles adsorbed directly on the Pt surface should be highly oriented at potentials away from the p.z.c. (13,14), so that

the molecules which rotate are possibly in the diffuse layer. This model also explains the concentration dependence. As the solution becomes more dilute, there are fewer ions, resulting in a more loose structure in the double layer, and thus longer times are required to orient the water dipoles completely. The similarity in perturbation times for K^+, Rb^+, and Cs^+ are well in agreement with the suggested negative hydration or structure-breaking properties of larger cations. Anions, which are not strongly hydrated, would thus not be expected to influence the perturbation times in this model.
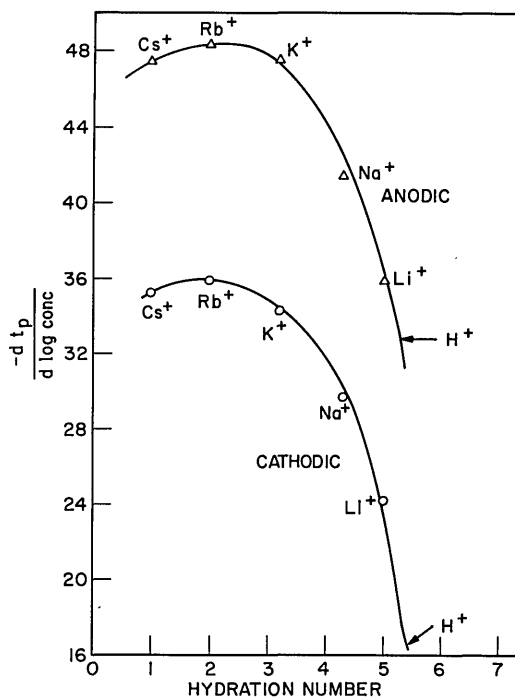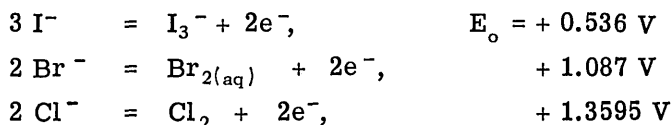

Fig. 8 - Change in perturbation time with concentration, $-dt_p/d \log conc$, versus hydration number (11)

The one experimental observation which is completely contrary to this model and which cannot be explained is that of the current independence of t_p. If the process occurring during the transition time is the orientation of dipoles, and if double-layer charging begins when this orientation is essentially complete, i.e., when the dielectric is saturated, then t_p would have to depend on the amount of charge flowing into the double layer. Any model which proposes the completion of a process in the compact layer before the double layer begins to charge up must be dependent on charge, and hence t_p would have to change with charging-current density. For a given system, t_p was found to be independent of the charging current over more than one order of magnitude. The apparent independence of t_p on the reversible potential could also argue against this model. For example, for 1 M systems of KI/I_2, KBr/Br_2, and KCl/Cl_2, the reversible potentials differ by about 1 V, as seen from the following equilibria (15).

$$3 I^- = I_3^- + 2e^-, \qquad E_o = + 0.536 \text{ V}$$

$$2 Br^- = Br_{2(aq)} + 2e^-, \qquad + 1.087 \text{ V}$$

$$2 Cl^- = Cl_2 + 2e^-, \qquad + 1.3595 \text{ V}$$

It is expected that a shift of potential difference across the double layer would strongly
affect the structure of the adsorbed layer and orientation of water dipoles. The possibility
does exist that the p.z.c. would shift in such a direction to balance this change in equilibrium
potential. Recent determinations of the p.z.c. of Pt in halide solutions using radiotracer
methods indicate that the p.z.c. does shift in the positive direction in going from I^- to Cl^-
solutions, possibly by as much as 0.7 V (16). The change in equilibrium potential could
therefore be accompanied by a corresponding shift in p.z.c. such that the double-layer
structure would not be appreciably altered. In the absence of more detailed information,
this point will not be further considered except to indicate that it need not be a serious
consideration.

In a recent study, Grantham (17) has concluded that there is a complete absence of
relaxation times of water molecules in the double layer in the range 10^{-8} to 10^{-2} sec, and he
attributes the observed frequency dependence of resistance and capacitance to improper
electrode design. On the basis of this and other studies (18-22), Devanathan (5) concludes
that water molecules are not oriented in up-and-down positions (14), but are adsorbed flat
and are insensitive to field. This conclusion seems premature with the lack of evidence
on ac frequency variation of the double-layer resistance and capacitance at frequencies
above about 10^5 cps on solid electrodes, which is just the range where the relaxation pro-
cess should become important, and particularly in light of the success which the water di-
pole model has had in interpreting organic adsorption. On the basis of the previous argu-
ment our results suggest that it is not the saturation of dielectric constant as brought about
by dipole orientation which determines the perturbation time. However, our results do
definitely establish that a perturbation time exists which may be similar to the frequency
variation observed in ac impedance measurements, and the rotation of dipoles should not
be ruled out, even though t_p is not determined by such a process.

A model which permits a t_p independent of charge is based on the specific adsorption
of ions, particularly anions. We first postulate, in line with earlier reasoning, that two
fundamentally different processes occur, the first of which is the means by which charge
is used up without actual charging of the double layer and may include more than one
type of process, i.e., dipole orientation, charge transfer, ion movement within solvation
sheaths, etc., and the second of which involves the movement of ions into or out of the
compact layer and determines t_p. The first process has been considered on a physical
basis, and we shall now examine it in greater detail. Following the double-layer model of
Grahame (6), the charge on the metal will equal the sum of charges in the inner and outer
Helmholtz layers and the charge in the diffuse layer:

$$-q_M = q_i + q_o + q_d$$

where the q's will be negative for anions and positive for cations. In the presence of spe-
cific adsorption, which is expected for the systems examined here, there will be additional
charge in the inner layer and hence also in the outer layer to maintain a constant q_M at a
given potential difference (with respect to the p.z.c.), i.e., superequivalent or contact ad-
sorption. Thus ions could undergo discharge in the inner layer and a corresponding trans-
fer of oppositely charged ions out of the outer layer, or possibly only a shift of the outer
Helmholtz plane would maintain constant q_M. Charge transfer, which could be a fast pro-
cess from ions already present in excess in the inner layer, with a corresponding shift
of the outer Helmholtz plane could therefore occur while the charge on the metal remains
constant, and thus energy could be used up without actual charging of the double-layer
capacitor.

Two cases should be distinguished, one for electrodes positive to the p.z.c., which is
the case for most of the equilibrium systems considered here, and one for electrodes neg-
ative to the p.z.c., which is probably the case for reversible hydrogen systems on Pt. In
the first case, an anodic pulse would require electron transfer from anions specifically

adsorbed on the Pt, with a simultaneous shift of cations within their hydration sheaths away from the electrode. The actual movement of cations during this time may be suggested; however, in view of the proposal that the perturbation time is determined by the time required for appreciable movement of ions into the double layer, this movement would seem less likely than the smaller movement of many cations corresponding to a single anion discharge. A cathodic pulse would then require reduction of atoms to anions in the inner layer, with a corresponding movement of the outer Helmholtz plane toward the electrode surface. Since the amounts of specifically adsorbed ions become appreciable, particularly for the halide systems (23), this process would not be limited by the charging current in the times under consideration. For the second case, i.e., electrode surface negative to the p.z.c., an anodic pulse would require discharge of atoms to form cations (probably $H \rightarrow H^+ + e^-$) with a subsequent shift of anions away from the electrode. A cathodic pulse would then involve electron transfer to H^+ to form H atoms and movement of anions toward the surface.

Following a recent suggestion by Delahay (24), the amounts of specifically adsorbed ions participating in this process can be examined using the relation:

$$q_{measured} = q + \frac{V_{sr}}{V_{sr} + V_{tr}} \cdot ZF\Gamma$$

where q is that charge due to the usual double-layer charging process, and the other term is due to a Faradaic process, where V_{sr} is the rate of the charge-separation process and V_{tr} is the rate of the mass-transfer process. During t_p, q = O, so that from the charging current and t_p, the surface excess should be obtained directly. For typical values of i = 1 A/cm2 and t_p = 100 nanosec, we obtain $ZF\Gamma_- = 0.1 \mu$ coul/cm^2, assuming that V_{tr}, the term relating to mass transfer, is zero, since mass transfer has not yet begun. This calculation gives a surface excess of $\Gamma_- = 10^{-12}$ g-eq/cm^2 for anions involved in the Faradaic process, and if we assume that cations are pushed out of the double layer, a Γ_+ of 10^{-12} g-eq/cm2 would be required. This value compares well with the Γ_+ reported from radiotracer measurements on Pt electrodes for alkali-halide systems (16). At high enough current densities, essentially all of the superequivalently adsorbed anions, i.e., those adsorbed in excess of the amount expected on the basis of the charge on the metal surface and hence balanced by cations in the outer Helmholtz plane and the diffuse layers, should be used up in the Faradaic process. Thus at high enough current densities, this method should be suitable for determining directly the amount of superequivalent or contact adsorption.

This process should not be particularly sensitive to the ions in solution, so long as they are adsorbed in sufficient excess to satisfy the charge requirements during the perturbation time and provided the rate of electron transfer is sufficiently fast. The cation effect must be explained in terms of the second process, i.e., in terms of the actual movement of ions into or out of the double layer. These two processes should not be viewed as occurring exclusively; some diffusion will begin during t_p, and only when appreciable mass transfer can occur does the potential begin to change. The fact that both processes occur together is seen from the slight curvature in the charging curves between the flat initial region and the linear double-layer charging region. The manner in which cations can influence the diffusion process is difficult to see; however, their influence is an experimental fact. The effect of cations is most probably related to hydration and the structure of the solution as already discussed.

SUMMARY

The experimental observations obtained using the discussed short-pulse technique are new and perhaps somewhat difficult to accept in light of the commonly accepted concepts of the double-layer structure. However, when comparisons are made with well-established relaxation times observed in bulk solution, the results appear reasonable. It should be

remembered that the results refer to events in the double layer which occur before the charging process and which have not been previously examined. Further, it should be remembered that every effort was made to eliminate instrumental artifacts, and we feel that the results presented reflect actual properties of the double layer. The model proposed has limitations, but it does essentially account for the experimental observations. Further measurements, particularly using doubly and triply charged cations, are required before a more detailed model can be proposed. These results tend to confirm the recent suggestion of Delahay that two processes can occur in the charging process; however, they suggest that the Faradaic contribution is less than 1 percent of the total charge. Finally, these results point to the discrete-particle nature of the electrical double layer, and the method holds real promise for obtaining more detailed information about the structure of the double layer at electrodes.

ACKNOWLEDGMENT

REFERENCES

1. Schuldiner, S., and Presbrey, C.H., Jr., "Short-Pulse Techniques, Part 1 - Kinetics of the Triiodide/Iodide Reaction on a Platinum Electrode in Neutral Solution," NRL Report 5978, Aug. 20, 1963; J. Electrochem. Soc. 111:457 (1964)

2. Presbrey, C.H., Jr., and Schuldiner, S., "The Application of an X-Y Pulsed Measuring System to Polarization Studies, Part 1 - The Hydrogen Reaction on Platinum," NRL Report 5616, July 27, 1961; J. Electrochem. Soc. 108:985 (1961)

3. Schuldiner, S., and Warner, T.B., "A Study of Adsorption and Oxidation of Carbon Monoxide on Platinum Using Constant-Current Pulses," NRL Report 6058, Apr. 24, 1964; J. Phys. Chem. 68:1223 (1964)

4. Schuldiner, S., and Roe, R.M., J. Electrochem. Soc. 110:332 (1963)

5. Devanathan, M.A.V., and Tilak, B.V.K.S.R.A., Chem. Rev. 65:635 (1965)

6. Grahame, D.C., Chem. Rev. 41:441 (1947)

7. Bockris, J.O'M., Mehl, W., Conway, B.E., and Young, L., J. Chem. Phys. 25:776 (1956)

8. Bockris, J. O'M., and Conway, B.E., J. Chem. Phys. 28:707 (1958)

9. Narayan, R., Venkatesan, V.K., and Doss, K.S.G., J. Sci. Industr. Res. 20B:450 (1961)

10. Kavanau, J.L., "Water and Solute-Water Interactions," Holden-Day, Inc., San Francisco (1964)

11. Andersen, T.N., and Bockris, J. O'M., Electrochim. Acta 9:347 (1964)

12. Samoilov, O. Ya., Disc. Faraday Soc. 24:141 (1957)

13. Mott, N.F., and Watts-Tobin, R.J., Electrochim. Acta 4:79 (1961)

14. Bockris, J. O'M., Devanathan, M.A.V., and Muller, K., Proc. Roy. Soc. 274:55 (1963)

15. de Bethune, A.J., and Swendeman Loud, N.A., "Standard Aqueous Electrode Potentials and Temperature Coefficients at 25°C," Clifford A. Hampel, Skokie, Ill. (1964)

16. Balashova, N.A., and Kazarinov, V.E., Elektrokhimiya 1:512 (1965)

17. Grantham, D.H., Ph. D. Dissertation, Iowa State U., Ames, Iowa (1962)

18. Damaskin, B.B., Zh. Fiz. Khim. 32:2199 (1958); Russ. Chem. Rev. 30:78 (1961)

19. Grahame, D.C., J. Am. Chem. Soc. 68:301 (1946)

20. Lorenz, W., Z. Physik. Chem. 26:424 (1960)

21. Melik-Gaikazyan, V.I., Zh. Fiz. Khim. 26:560 (1952)

22. Melik-Gaikazyan, V.I., and Dolin, P.I., Dokl. Akad, Nauk SSSR 66:409 (1949)

23. Wroblowa, H., Kovac, Z., and Bockris, J. O'M., Trans Faraday Soc. 61:1523 (1965)

24. Delahay, P., Preprints of Symposium on Electrode Processes, p. 1, Electrochem.
     Soc. Annual Meeting, Cleveland, May 1966

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Naval Research Laboratory Washington, D.C. 20390	Unclassified
	2b. GROUP

3. REPORT TITLE

SHORT-PULSE TECHNIQUES, PART 2 - PERTURBATION TIMES IN ALKALI-HALIDE SYSTEMS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

An interim report on the problem.

5. AUTHOR(S) (First name, middle initial, last name)

Bernard J. Piersma, Sigmund Schuldiner, and Theodore B. Warner

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
January 17, 1967	18	24

8a. CONTRACT OR GRANT NO. NRL Problems C05-06 and C05-13 b. PROJECT NO. SR 007-12-01-0809 c. RR 001-01-43-4754 d.	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6458 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Department of the Navy (Naval Ship Systems Command, Office of Naval Research)

13. ABSTRACT

A new technique involving the perturbation of a system from equilibrium using very short galvanostatic pulses and miniature cells has been applied to study of the electrical double layer at Pt electrodes. The perturbation time, the time required for the double layer to begin charging, was determined for hydrogen- and alkali metal-halide systems and for reversible hydrogen systems in several acids and NaOH. The perturbation time was essentially independent of charging-current density and of the anion in solution but was strongly dependent on the cation species and electrolyte concentration. Models to explain the absence of electrode polarization during the initial flow of charge into the double layer are discussed. A model which involves a very fast Faradaic process and which is consistent with the experimental observations is proposed. It is suggested that the perturbation time, which is less than 100 nanosec for 1 M solutions, represents the time required for movement of ions into or out of the compact double layer.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Platinum electrodes, polarization Double layer, structure of Galvanostatic study of double layer Electrochemistry						